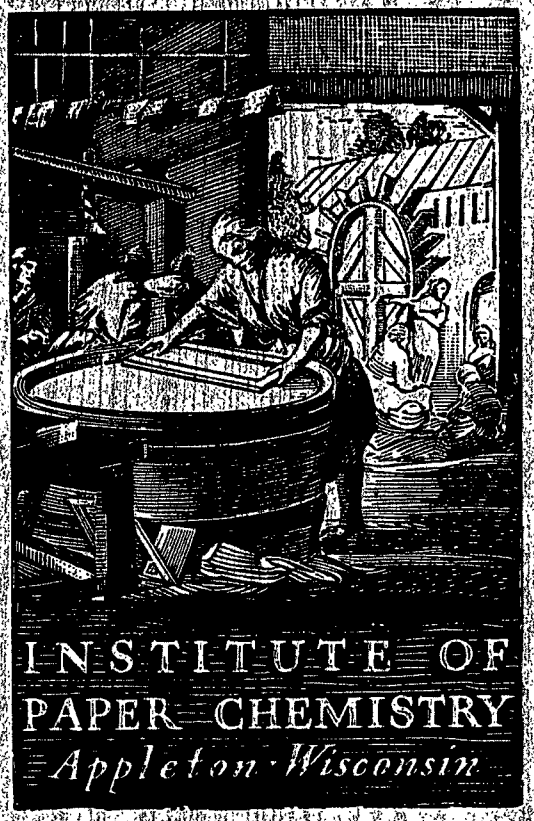

LIQUOR CONDITIONS IN KAMYR CONTINUOUS DIGESTERS

Project 3552

Final Report
A Progress Report
to
DIGESTER CRACKING RESEARCH COMMITTEE

August 15, 1984

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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ABSTRACT

The compositions of kraft cooking liquors were determined at various sites in five Kamyr continuous digesters to supplement liquor analyses reported in a previous study. At each mill, liquors were sampled at five sites to characterize changes in the liquor strength at various stages of pulping; samples included raw white liquor, make-up liquor, top circulation liquor, impregnation zone liquor, and upper cook zone liquor.

Hydroxyl ions were apparently consumed at the various stages by low temperature cooking processes, but the other major and minor constituents remained essentially unchanged at the five sites examined, aside from some initial dilution effects. However, hydrolysis of sulfide ion will replace some of the hydroxyl ion removed by cooking processes, but the extent of hydrolysis is not known. Vessels with severe cracking operated with as little as 40 g/L (as Na_2O) active alkali at the site of cracking.

As in the initial study, no correlations were found between digester cracking susceptibility and the inorganic composition of liquors extracted from that vessel. Seasonal fluctuations in cracking susceptibility at one mill could not be related to seasonal changes in the composition of the liquor.

Make-up liquors examined in the initial study are likely to contain somewhat higher concentrations of active alkali, but otherwise are similar to liquors found in the impregnation zone at the site of cracking.

EXECUTIVE SUMMARY

A supplementary study was performed by The Institute of Paper Chemistry to characterize the liquor conditions existing in Kamyr continuous digesters. Liquors were obtained from various locations in the process streams at five different mills, and these liquors were analyzed to determine the concentrations of inorganic species present in the liquors. The liquors were analyzed in the same manner as in the preceding Institute project on continuous digester cracking.

Several objectives were pursued in this study. The first objective was to determine the composition of liquors in contact with the vessel wall at the site where cracking has been most severe — in the impregnation zone. Previous samples were not taken from this zone because of concerns about safe extraction of liquors from high pressure ports. A related objective was the comparison of liquor compositions in the impregnation zone and the make-up liquor pump suction (where samples had been taken and electrochemical tests had been conducted in the preceding study). A third objective was to determine if the liquors in the impregnation zone of digesters with severe cracking differed from those in digesters with no evidence of cracking to date. Finally, liquors were sampled in winter and summer seasons at one mill where seasonal fluctuations and cracking susceptibility had been reported, in an attempt to identify liquor characteristics that promote digester cracking.

The conclusions of this study are as follows:

1. The concentration of the hydroxyl ions thought to be responsible for digester cracking is reduced from white liquor levels by dilution and by consumption in low temperature cooking processes. The concentration of NaOH

ecreases at various sites in the following order: raw white liquor, make-up iquor, top recirculation liquor, impregnation zone liquor, and upper cook zone iquor. The concentrations of the other inorganic constituents present in ooking liquor remained approximately constant, once dilution of raw white liquor had occurred in the process.

2. Hydrolysis considerations and the inability of the acidimetric titration to resolve the extent of hydrolysis cloud the measurement of the exact concentration of hydroxyl ions in the impregnation zone liquors. However, it is expected that, as hydroxyl ions are consumed by low temperature cooking, they will be replaced to some extent by a hydrolysis reaction that converts S^{--} ions to HS^- and additional OH^- ions. Therefore, the effective alkali concentration appears to be more indicative of the driving force for cracking than the measured OH^- concentration.

3. Cracking susceptibility was not related to the inorganic composition of the liquors present at the impregnation zone during three successive days of sampling. It appears that both cracked and uncracked digesters have liquors whose compositions will support cracking if the other conditions for cracking are satisfied. These conditions include a high tensile stress, a susceptible metallurgical structure, access of the liquor to the metal, and development of an appropriate electrochemical potential at the steel/liquor interface.

4. Seasonal differences in cracking susceptibility at the selected mill could not be related to differences in the concentrations of inorganic constituents of winter and summer liquors.

INTRODUCTION

The Institute of Paper Chemistry (IPC) recently completed an investigation of continuous digester conditions that influence the degree of cracking susceptibility in Kamyr continuous digesters. Various aspects of digester fabrication and operation were considered, including a detailed investigation of the inorganic composition of liquors extracted from digesters with severe cracking and those without cracking. Several weak correlations were identified which increased the risk of severe cracking. A report (1) of the results was distributed to the members of the Digester Cracking Research Committee contributing to the support of the project. The conclusions were also summarized in a presentation to the TAPPI Engineering Conference (2) and in an article published in Pulp and Paper Magazine (3).

There was little evidence in the initial investigation to indicate that the composition of cooking liquors sampled and analyzed during this investigation had a significant effect on cracking susceptibility. A survey showed that the target alkalinity and sulfidity of the white liquor used in the digestion process did not correlate with cracking susceptibility in North American digesters. Furthermore, a detailed comparison of liquor conditions in three vessels with severe cracking and three vessels with apparent immunity failed to reveal differences that were linked to cracking susceptibility. Analyses of the inorganic compositions of liquors extracted at these mills failed to reveal an effect of concentration of major, minor, or trace constituents in either white liquor or liquors extracted from the make-up liquor line. Electrochemical studies conducted in the liquors at six mills also failed to reveal a difference in behavior that was associated with cracking susceptibility.

The inability to link liquor conditions with cracking susceptibility in this study can be explained in various ways. For example, there may actually be no link between cracking and liquor composition and the results of the study represent the actual circumstance. Alternatively, there may be some interaction between liquor composition and cracking susceptibility, but it was not discovered in the investigation for one of a variety of reasons. Cracking may be occurring only as a result of upset conditions — during start-up or shut-down, for example — which were not examined in the study. On the other hand, the organic compounds present in liquors may control cracking, but techniques were not available for routine analysis of these compounds. Finally, liquors were not actually sampled from the impregnation zone where cracking is most prevalent, and differences may exist between the sampling site (at the make-up liquor pump) and the impregnation zone.

Addressing the latter point, most of the liquors sampled and analyzed in the original study were taken either from the raw white liquor supply or from the make-up liquor line at the make-up liquor pump suction. The make-up liquor line was chosen for safety reasons as the sampling site to avoid tapping high pressure lines, while retaining some proximity to the impregnation zone in the actual digester. There is extensive intermingling of liquors from the top recirculation line, the liquid-level control line, and the make-up liquor line in the Kamyr digester system. It was postulated, but not proven, that liquors in the impregnation zone would be similar to those obtained at the make-up site because of this intermixing process. However, some low temperature cooking was thought to occur during contact between chips and liquor, and this cooking was thought to deplete the NaOH content of the impregnation zone liquor. Consequently, there was some concern that the liquors sampled in the original study

were not representative of conditions in the impregnation zone where cracking was most prevalent.

To resolve this concern, additional measurements were made to determine the inorganic composition of liquors taken from various points in the Kamyr system at several mills. Samples were extracted from high pressure sampling sites by Kamyr, Inc. field engineers to allay concerns about safety. Liquors were sampled at five different mills, including some of the mills sampled in the initial study (Mill Codes 60, 62, 110). Liquors were taken from four locations at the same time on three successive days; sampling sites included (1) raw white liquor (WL), (2) make-up liquor taken at the make-up liquor pump suction (MLP), (3) top circulation liquor taken at the top circulation line vent adjacent to the top separator (TC), and (4) upper cook zone liquor taken at the suction of the upper cook zone recirculation pump (UC). At one mill where a two-vessel system was in operation, bottom circulation liquor was taken in place of upper cook liquor (BC). At two mills, liquors were actually extracted from the impregnation zone of the digester at sampling points installed by the mill for that purpose (IZ). The sampling sites are shown schematically in Fig. 1.

These liquors were treated and analyzed in the same fashion as liquors taken in the initial study, except that trace elements were not determined. The liquors were analyzed for the following inorganic species: NaOH, Na_2S, Na_2S_x, Na_2CO_3, Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4, and NaCl. As before, the complexity of the organic compounds present precluded meaningful analysis of organic constituents with the time and funds available.

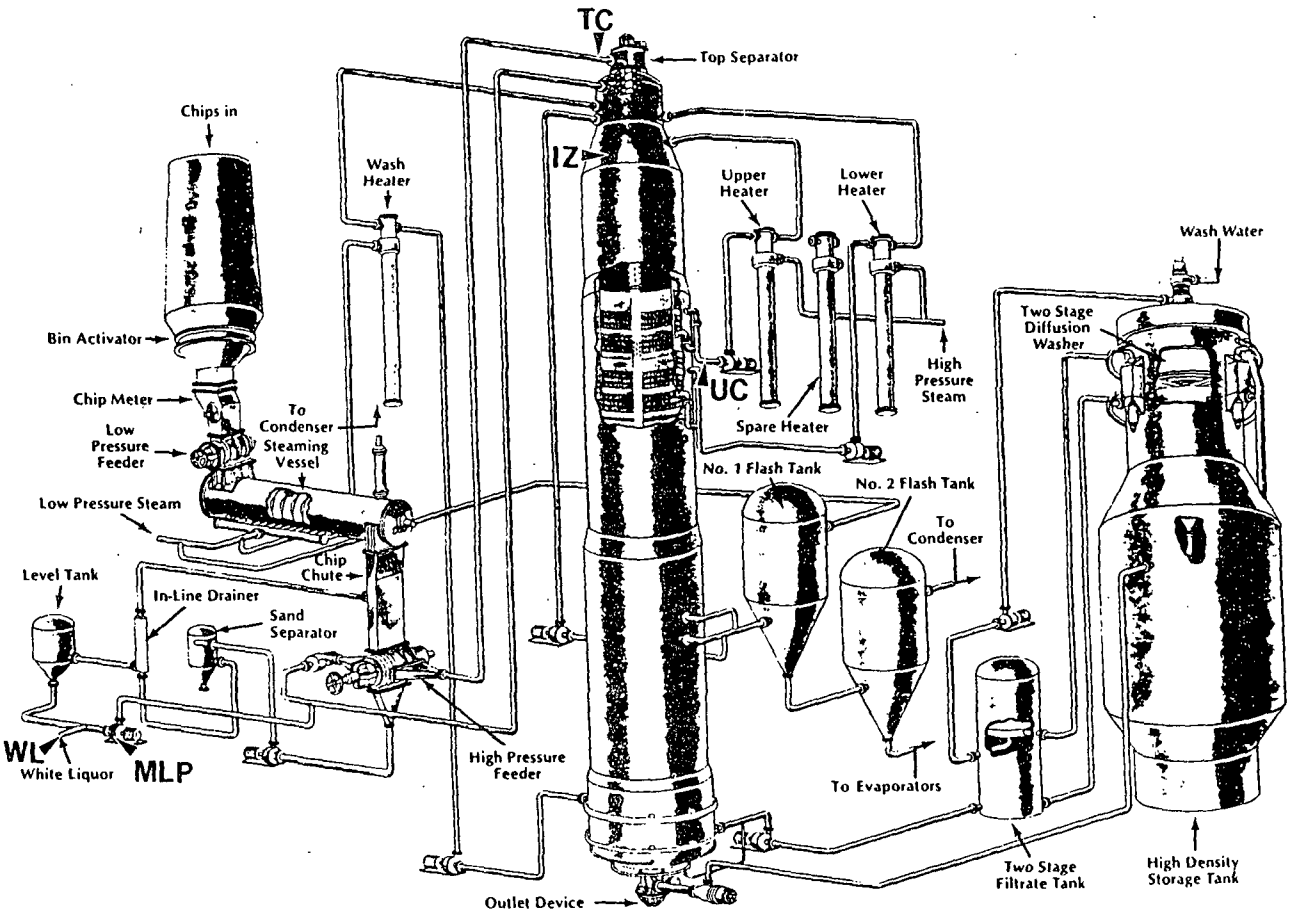

Figure 1. Sample location sites shown schematically on hydraulic digester layout (figure printed with permission of Kamyr, Inc.).

The choice of sampling sites provided an assessment of changes in liquor composition at successive stages in continuous digester operation. The profile of liquor composition in the impregnation zone where cracking is most severe was evident from samples taken at top circulation, impregnation zone, and upper cook sampling sites. Furthermore, the value of the original study on make-up liquors was evaluated by comparison of impregnation zone liquors with make-up liquors taken at the same point in time. Finally, this supplementary program provided a better estimate of digester conditions for use in laboratory

simulation in DCRC programs conducted at the Pulp and Paper Research Institute and Battelle Columbus Laboratories.

At one mill (Mill 212), two samples were taken approximately six months apart to search for differences in liquor that would explain seasonal variations in cracking severity at this mill. Periodic inspections of the welds in this vessel have shown that cracking is much more severe during operation through the winter months, compared to summer operation. The composition of the liquor is adjusted seasonally to accommodate changes in chip furnish in summer and winter months, principally by changing the amount of black liquor added to the make-up liquor. Samples were taken during winter and summer operation to determine if differences in composition could be related to cracking susceptibility.

PROCEDURES

Wherever possible, the procedures for sampling and liquor analysis used in the initial study were also employed in the supplementary study reported here.

Liquors were obtained by Kamyr, Inc. field engineers at each site, following a procedure established at the first mill visit. Samples of liquor were obtained by opening the appropriate valve to admit the liquor to a hose and a nearby receptacle. Flashing of the upper cook zone liquor was prevented by first passing the liquor through a stainless steel cooling coil. A sample of each of the liquors was captured in a polypropylene bottle which was filled by submersion in the liquor as soon as a sufficient level was achieved. To avoid entrainment of air in the sample bottle, the sample bottle was sealed under the liquor level by the Kamyr engineer wearing rubber gloves. Samples were taken daily for three days from each of the sampling sites and then sent to IPC for analysis via air express shipment. Previous studies indicated that the samples were stable in inorganic composition for as long as two weeks, provided air was excluded from the sample bottle.

When the liquors arrived at IPC, they were divided into several smaller bottles for individual analytical tests. This division was accomplished in a glove bag filled with nitrogen gas to prevent oxidation of the reduced sulfur compounds. All samples were stored in completely filled vials or in vials with nitrogen gas in the plenum above the liquid.

The concentrations of NaOH, Na_2S, and Na_2CO_3 were determined by (ABC) acidimetric titration to pH end-points of 9.3 (A), 8.3 (B), and 4.0 (C). This is the procedure used in the initial study.

Polysulfide concentration was determined by a potentiometric titration using a sulfide-sensitive, ion selective electrode, in a procedure commonly known as the Mead Amalgam method. The liquors were treated by a short exposure to a sodium amalgam to reduce polysulfide to sulfide, leaving the less-reactive sulfoxy compounds largely unchanged. Polysulfide was then determined by the difference in sulfide concentration in liquors with and without sodium amalgam pretreatment. This test also provided a check on the sulfide determination made by the acidimetric titration. Again, this procedure was the same as that used in the initial study.

The concentrations of sulfoxy compounds — $SO_3^=$, $SO_4^=$ and $S_2O_3^=$ — and Cl^- were determined by an ion chromatographic method, using the procedures involved in the initial study. Duplicate runs were made at an independent testing laboratory to validate the results.

All species except polysulfide are reported as sodium salt concentration in grams per liter (as chemical, not Na_2O equivalent).

The mill code identification numbers and several details of mill operation at the mills are shown in Table 1. Liquors from Mills 60, 62, and 110 were sampled in the first study and these mills retain the same identification number. Mills 201 and 212 were not sampled in the previous study, but were added because of their capability of impregnation zone sampling.

Table 1. Mills providing liquors in the second study.

Mill Code	Pulping Conditions	Nominal Sulfidity, %	Active Alkali	% on Wood	Top Circ Temp.	Kappa No.	Upper Cook Residual	Extraction Residual	Cracking
212 (summer)	~ 1100 ADT/day	30-33	5.7-5.8#/ft^3	17-18 AA	240-251°F	20-31	1.64-1.71#/ft^3 AA	--	Yes[a]
212 (winter)	~ 1100 ADT/day	31-33	6.0-6.2	18.5-18.7 AA	239-240	18-27	1.69-1.85#/ft^3 AA	--	Yes[a]
62	~ 600 ADT/day AG. Hwd./Swd.	25-26	6.1-6.4	17.5-18 AA	260-265	11 (Hwd.)-25 (Swd.)	--	0.64-0.80#/ft^3 AA	No
60	~ 500 ADT/day AH. Hwd./Swd.	25-27	6.2-6.7	12% EA (Swd.) 15% EA (Hwd.)	239-241	12 (Hwd.)-25 (Swd.)	--	--	No
110	270 ADT/day	19-20		16-17	240-245	18-22	--	--	No
201	470 ADT/day, two vessel	23-26	5.4-5.6 EA	14.8-15 EA	228	26-30	--	9.0-9.7 g/L	Yes

[a]Reduced cracking susceptibility reported during summer months.

RESULTS

Tables 2 and 3 show the concentration of major and minor compounds present in the liquor analyzed in the supplementary program. All concentrations are given as grams per liter of the sodium compound as chemical, not equivalent Na_2O, except polysulfide which was given as grams/liter of excess elemental sulfur present in the liquor. The average concentration of the liquors is given in Table 4 to show trends in liquor composition at various mills and at various locations in the continuous digester process stream.

The composition of the white liquors analyzed is well within the range of common practice in the kraft pulping industry (4). The concentration of sodium hydroxide averaged over three days ranged from 83 g/L at Mill 212 (summer) to 95 g/L at Mill 201. The highest concentration of NaOH measured in white liquor was 101 g/L while the lowest concentration was 81 g/L, which constitutes a variation of only 20 g/L (approximately 20%) at the five mills surveyed. The sodium sulfide concentration averaged over three days varied to a greater extent from mill to mill, ranging from 21 g/L at Mill 110 to 44 g/L at Mill 212 (winter). As shown in Table 4, the average active alkali varied from 84 to 102 g/L (Na_2O) and the average sulfidity ranged from 19 to 35% (AA basis). The sodium carbonate concentration varied from 17 to 29 g/L at the five mills surveyed. The concentrations of the major species — NaOH, Na_2S, and Na_2CO_3 — are well within the range typically reported for kraft white liquors (4,5).

Table 2. Major liquor concentrations (g/L) as chemical.

Rec. No.	Mill	Site	Date	CRA	NaOH	Na_2S	Na_2CO_3	Na_2S/NaOH
1	201	WL	5/6/83	CR	94.6	33.4	26.5	0.35
2	201	MLP	5/6/83	CR	55.9	21.3	19.5	0.38
3	201	TC	5/6/83	CR	49.4	20.2	19.0	0.41
4	201	IZ	5/6/83	CR	48.8	19.9	19.1	0.41
5	201	BC	5/6/83	CR	21.7	16.2	21.6	0.75
6	201	WL	5/7/83	CR	95.7	34.8	21.3	0.36
7	201	MLP	5/7/83	CR	55.6	23.3	17.2	0.42
8	201	TC	5/7/83	CR	51.3	20.8	16.5	0.41
9	201	IZ	5/7/83	CR	50.4	21.6	16.4	0.43
10	201	BC	5/7/83	CR	22.2	16.8	19.4	0.76
11	201	WL	5/8/83	CR	94.0	38.5	28.8	0.41
12	201	MLP	5/8/83	CR	58.7	26.0	21.6	0.44
13	201	TC	5/8/83	CR	51.5	23.7	20.6	0.46
14	201	IZ	5/8/83	CR	50.6	23.6	20.3	0.47
15	201	BC	5/8/83	CR	21.5	18.3	22.0	0.85
16	212	WL	5/11/83	NC?	82.6	36.7	16.6	0.44
17	212	MLP	5/11/83	NC?	53.7	28.1	13.9	0.52
18	212	TC	5/11/83	NC?	43.2	24.9	13.4	0.58
19	212	IZ	5/11/83	NC?	32.7	22.8	14.2	0.70
20	212	UC	5/11/83	NC?	13.3	19.3	15.6	1.45
21	212	WL	5/12/83	NC?	81.1	39.9	19.8	0.49
22	212	MLP	5/12/83	NC?	56.1	30.5	16.8	0.54
23	212	TC	5/12/83	NC?	44.3	26.4	15.3	0.60
24	212	IZ	5/12/83	NC?	27.2	23.2	16.6	0.85
25	212	UC	5/12/83	NC?	16.2	21.2	17.2	1.31
26	212	WL	5/13/83	NC?	85.1	41.9	20.7	0.49
27	212	MLP	5/13/83	NC?	55.2	31.6	17.2	0.57
28	212	TC	5/13/83	NC?	45.1	27.6	16.5	0.61
29	212	IZ	5/13/83	NC?	29.8	24.5	17.1	0.82
30	212	UC	5/13/83	NC?	13.1	21.8	18.0	1.66
31	060	WL	5/24/83	NC	99.3	35.5	24.0	0.36
32	060	MLP	5/24/83	NC	74.5	29.8	22.5	0.40
33	060	TC	5/24/83	NC	56.3	24.8	21.1	0.44
34	060	UC	5/24/83	NC	17.9	18.3	22.7	1.02
35	060	WL	5/25/83	NC	100.6	34.5	19.8	0.22
36	060	MLP	5/25/83	NC	74.9	27.9	18.4	0.34
37	060	TC	5/25/83	NC	61.9	24.7	18.4	0.40
38	060	UC	5/25/83	NC	25.4	21.0	29.1	0.83
39	060	WL	5/26/83	NC	95.9	34.3	27.8	0.36
40	060	MLP	5/26/83	NC	70.7	28.8	25.9	0.41
41	060	TC	5/26/83	NC	57.6	24.8	25.3	0.43
42	060	UC	5/26/83	NC	17.7	18.8	31.6	1.06
43	110	WL	6/14/83	NC	84.5	20.7	27.2	0.24
44	110	MLP	6/14/83	NC	48.7	15.8	26.2	0.32
45	110	TC	6/14/83	NC	55.5	16.6	26.7	0.30
46	110	UC	6/14/83	NC	21.9	13.1	29.7	0.60

Table 2 (Contd.). Major liquor concentrations (g/L) as chemical.

Rec. No.	Mill	Site	Date	CRA	NaOH	Na_2S	Na_2CO_3	Na_2S/NaOH
47	110	WL	6/15/83	NC	89.0	20.4	23.2	0.23
48	110	MLP	6/15/83	NC	53.1	15.1	23.1	0.28
49	110	TC	6/15/83	NC	53.5	16.2	25.1	0.30
50	110	UC	6/15/83	NC	21.1	13.0	28.6	0.62
51	110	WL	6/16/83	NC	89.1	20.6	25.0	0.23
52	110	MLP	6/16/83	NC	64.6	17.1	22.9	0.26
53	110	TC	6/16/83	NC	65.1	17.3	23.6	0.27
54	110	UC	6/16/83	NC	22.0	13.7	29.3	0.62
55	62	WL	7/19/83	NC	90.0	32.0	27.4	0.36
56	62	MLP	7/19/83	NC	56.3	24.7	26.7	0.44
57	62	TC	7/19/83	NC	43.4	22.4	27.0	0.52
58	62	UC	7/19/83	NC	16.8	17.6	29.7	1.05
59	62	WL	7/20/83	NC	89.5	32.1	28.6	0.36
60	62	MLP	7/20/83	NC	55.8	24.5	28.2	0.44
61	62	TC	7/20/83	NC	48.3	22.4	28.1	0.46
62	62	UC	7/20/83	NC	14.7	17.5	30.9	1.20
63	62	WL	7/21/83	NC	89.4	31.8	29.7	0.36
64	62	MLP	7/21/83	NC	67.8	27.1	30.6	0.40
65	62	TC	7/21/83	NC	57.4	25.2	31.3	0.44
66	62	UC	7/21/83	NC	20.6	19.3	34.4	0.90
67	212	WL	1/4/84	CR?	84.4	42.5	21.6	0.50
68	212	MLP	1/4/84	CR?	52.9	31.1	19.0	0.59
69	212	TC	1/4/84	CR?	42.5	27.8	19.2	0.65
70	212	UC	1/4/84	CR?	13.2	22.4	22.4	1.70
71	212	WL	1/5/84	CR?	83.8	45.0	23.9	0.54
72	212	MLP	1/5/84	CR?	54.7	33.4	20.7	0.61
73	212	TC	1/5/84	CR?	43.9	29.5	22.8	0.67
74	212	UC	1/5/84	CR?	14.1	23.2	23.9	1.65
75	212	WL	1/6/84	CR?	85.6	43.9	18.4	0.51
76	212	MLP	1/6/84	CR?	54.9	32.5	16.3	0.59
77	212	TC	1/6/84	CR?	42.9	28.5	16.3	0.66
78	212	IV	1/6/84	CR?	24.7	26.3	21.5	1.06
79	212	UC	1/6/84	CR?	--[a]	--[a]	--[a]	--[a]

[a]Line plugged — not available.

WL = White liquor.
MLP = Make-up liquor.
IZ = Impregnation zone liquor.
UC = Upper cook zone liquor.
BC = Bottom recirculation liquor (two vessel system).
CR = Severely cracked.
NC = No apparent cracking.
NC?,CR? = Seasonal dependence to cracking.

Table 3. Minor liquor concentrations (g/L) as chemical.

Rec. No.	Mill	Site	Date	CRA	NaCl	Na_2SO_3	$Na_2S_2O_3$	Na_2SO_4	S
1	201	WL	5/6/83	CR	2.5	5.1	8.0	20.0	0
2	201	MLP	5/6/83	CR	1.8	3.8	6.0	16.4	0
3	201	TC	5/6/83	CR	1.7	4.2	6.0	15.0	0
4	201	IZ	5/6/83	CR	2.1	4.0	5.7	14.7	0
5	201	BC	5/6/83	CR	1.4	3.0	4.4	12.3	0
6	201	WL	5/7/83	CR	1.3	7.9	8.7	18.7	0
7	201	MLP	5/7/83	CR	1.8	4.8	4.4	14.9	0
8	201	TC	5/7/83	CR	1.8	5.3	4.4	14.9	0
9	201	IZ	5/7/83	CR	1.7	4.9	4.1	14.5	0
10	201	BC	5/7/83	CR	1.6	5.8	4.4	12.6	0
11	201	WL	5/8/83	CR	2.7	9.0	7.2	15.3	0
12	201	MLP	5/8/83	CR	2.0	5.8	6.2	13.3	0
13	201	TC	5/8/83	CR	1.9	5.8	6.3	13.0	0
14	201	IZ	5/8/83	CR	1.9	4.9	5.9	12.3	0
15	201	BC	5/8/83	CR	1.5	5.4	5.1	10.7	0
16	212	WL	5/11/83	NC?	0.7	7.3	5.2	13.0	0.2
17	212	MLP	5/11/83	NC?	0.6	5.3	4.4	9.9	0.0
18	212	TC	5/11/83	NC?	0.4	8.7	5.9	10.6	0.0
19	212	IZ	5/11/83	NC?	0.5	9.2	6.5	10.2	0.0
20	212	UC	5/11/83	NC?	0.4	7.8	6.8	8.4	0.0
21	212	WL	5/12/83	NC?	0.8	6.0	6.1	7.5	0.1
22	212	MLP	5/12/83	NC?	0.5	8.1	5.6	6.0	0
23	212	TC	5/12/83	NC?	0.5	7.7	5.0	6.4	0
24	212	IZ	5/12/83	NC?	0.5	8.9	8.5	8.4	0
25	212	UC	5/12/83	NC?	0.4	7.5	7.0	6.6	0
26	212	WL	5/13/83	NC?	0.7	6.7	5.0	5.4	0.0
27	212	MLP	5/13/83	NC?	0.5	8.4	5.7	5.3	0
28	212	TC	5/13/83	NC?	0.5	8.1	6.1	4.8	0
29	212	IZ	5/13/83	NC?	0.5	7.1	5.6	5.1	0
30	212	UC	5/13/83	NC?	0.5	4.2	4.7	3.8	0
31	060	WL	5/24/83	NC	3.3	7.2	7.5	8.5	0.24
32	060	MLP	5/24/83	NC	2.9	11.3	10.6	13.7	0.00
33	060	TC	5/24/83	NC	2.5	7.9	9.4	8.9	0.00
34	060	UC	5/24/83	NC	2.0	3.6	6.2	5.5	0.00
35	060	WL	5/25/83	NC	3.0	9.2	7.8	8.4	0
36	060	MLP	5/25/83	NC	2.7	8.6	7.1	8.3	0
37	060	TC	5/25/83	NC	2.4	6.5	7.2	7.3	0
38	060	UC	5/25/83	NC	2.2	7.6	8.9	7.1	0
39	060	WL	5/26/83	NC	3.3	9.2	8.0	8.0	0
40	060	MLP	5/26/83	NC	2.8	8.2	6.6	7.5	0
41	060	TC	5/26/83	NC	2.5	6.3	7.0	7.1	0
42	060	UC	5/26/83	NC	2.1	2.8	5.6	5.4	0
43	110	WL	6/14/83	NC	8.7	4.0	4.4	5.8	0.00
44	110	MLP	6/14/83	NC	6.9	2.7	4.2	4.9	0.00
45	110	TC	6/14/83	NC	7.2	3.0	4.2	5.1	0.00
46	110	UC	6/14/83	NC	5.8	3.8	4.4	4.7	0.00

Table 3 (Contd.). Minor liquor concentrations (g/L) as chemical.

Rec. No.	Mill	Site	Date	CRA	NaCl	Na_2SO_3	$Na_2S_2O_3$	Na_2SO_4	S
47	110	WL	6/15/83	NC	8.9	3.7	4.4	5.7	0.0
48	110	MLP	6/15/83	NC	6.9	3.3	4.4	6.3	0
49	110	TC	6/15/83	NC	7.2	2.8	3.7	4.9	0
50	110	UC	6/15/83	NC	5.6	1.8	3.3	4.1	0
51	110	WL	6/16/83	NC	9.0	3.8	4.4	5.9	0.0
52	110	WLP	6/16/83	NC	7.7	3.0	4.1	5.6	0
53	110	TC	6/16/83	NC	7.8	4.2	5.0	7.1	0
54	110	UC	6/16/83	NC	5.8	2.8	3.5	4.4	0
55	62	WL	7/19/83	NC	6.6	2.6	4.8	4.5	0.1
56	62	MLP	7/19/83	NC	5.4	1.3	4.4	3.7	0.0
57	62	TC	7/19/83	NC	4.9	1.2	4.3	3.5	0.0
58	62	UC	7/19/83	NC	3.6	0.7	3.0	3.0	0.0
59	62	WL	7/20/83	NC	6.6	2.3	4.6	4.6	0.1
60	62	MLP	7/20/83	NC	5.0	1.4	4.6	3.8	0.0
61	62	TC	7/20/83	NC	4.6	2.0	5.0	3.7	0.0
62	62	UC	7/20/83	NC	3.6	2.0	3.5	3.0	0.0
63	62	WL	7/21/83	NC	6.5	2.4	4.8	4.8	0.0
64	62	MLP	7/21/83	NC	5.5	2.4	5.8	4.4	0.0
65	62	TC	7/21/83	NC	5.1	2.3	5.2	4.3	0.0
66	62	UC	7/21/83	NC	3.9	1.9	4.1	3.5	0.0
67	212	WL	1/4/84	CR?	0.7	10.8	7.4	5.7	0.0
68	212	MLP	1/4/84	CR?	0.6	8.7	7.4	6.4	0.0
69	212	TC	1/4/84	CR?	1.0	5.8	5.3	4.0	0.0
70	212	UC	1/4/84	CR?	0.5	3.4	4.6	3.7	0.0
71	212	WL	1/5/84	CR?	0.7	11.1	7.4	4.7	0.0
72	212	MLP	1/5/84	CR?	0.7	7.4	6.4	3.9	0.0
73	212	TC	1/5/84	CR?	0.6	6.2	6.4	4.3	0.0
74	212	UC	1/5/84	CR?	0.4	4.9	5.3	3.0	0.0
75	212	WL	1/6/84	CR?	0.7	10.7	7.4	6.0	0.0
76	212	MLP	1/6/84	CR?	0.5	5.6	6.7	4.4	0.0
77	212	TC	1/6/84	CR?	0.5	5.1	4.9	3.9	0.0
78	212	IZ	1/6/84	CR?	0.6	7.6	7.3	4.8	0.0
79	212	UC	1/6/84	CR?	--[a]	--[a]	--[a]	--[a]	--[a]

[a]Data unavailable — sample line plugged.

WL = White liquor.
MLP = Make-up liquor.
IZ = Impregnation zone liquor.
UC = Upper cook zone liquor.
BC = Bottom recirculation liquor (two vessel system).
CR = Severely cracked.
NC = No apparent cracking.
NC?,CR? = Seasonal dependence to cracking.

	NaOH, g/L	Na_2S, g/L	Na_2CO_3, g/L	NaCl, g/L	Na_2SO_3, g/L	$Na_2S_2O_3$, g/L	Na_2SO_4, g/L	AA, g/L	Sulfidity, %
201									
WL	94.8	35.6	17.1	2.2	5.7	8.0	18.1	102 (Na_2O)	28
MLP	56.7	23.5	19.4	1.9	4.9	5.5	14.9	63	30
TC	50.7	21.6	18.6	1.8	5.1	5.6	14.3	56	31
IZ	49.9	21.7	18.6	1.9	4.6	5.2	13.8	56	31
BC	21.8	17.1	21.0	1.5	4.7	4.6	11.9	30	45
212 (Summer)									
WL	82.9	39.5	20.3	0.8	6.7	5.4	8.6	96	33
MLP	55.0	30.1	16.0	0.5	7.3	5.2	7.1	67	36
TC	44.2	26.3	15.1	0.5	8.2	5.7	7.3	55	38
IZ	29.9	23.5	16.0	0.5	8.4	6.9	7.9	42	44
UC	14.2	20.8	16.9	0.5	5.1	6.0	6.3	28	59
60									
WL	98.6	34.8	23.9	3.2	8.5	7.8	8.3	104	27
MLP	73.4	28.8	22.3	2.8	9.4	8.1	9.8	80	29
TC	58.6	24.8	21.6	2.8	6.9	7.9	7.8	65	30
UC	21.7	19.4	27.8	2.1	4.7	6.9	6.0	32	48
110									
WL	87.5	20.6	25.1	8.9	3.8	4.4	5.8	84	19
MLP	58.0	16.7	25.1	7.4	3.3	4.3	5.7	58	23
TC	55.5	16.0	24.1	7.2	3.0	4.2	5.8	56	23
UC	21.7	13.3	29.2	5.7	2.8	3.7	4.4	27	39
62									
WL	89.6	32.0	28.6	6.6	2.4	4.7	4.6	95	27
MLP	60.0	25.4	28.5	5.3	1.7	4.9	4.0	67	30
TC	49.7	23.3	28.8	4.9	1.8	4.8	3.8	57	32
UC	17.4	18.1	31.7	3.7	1.6	4.2	3.2	29	52
212 (Winter)									
WL	84.6	43.8	21.3	0.7	10.9	7.4	5.5	100	35
MLP	54.2	32.3	18.7	0.6	7.2	6.8	4.9	68	38
TC	43.1	28.5	19.4	0.7	5.7	5.5	4.1	56	41
IZ	24.7	26.3	21.5	0.5	7.6	7.3	4.8	40	52
UC	13.7	22.8	22.8	0.5	4.2	5.0	3.4	29	63

The minor constituents of kraft white liquor that were analyzed were also within the range expected, with a few exceptions. The averaged Na_2SO_3 concentration ranged from 2 to 11 g/L, while the $Na_2S_2O_3$ concentration in white liquor averaged in the range 4 to 8 g/L. For four of the five mills surveyed, the Na_2SO_4 concentration was in the range, 5 to 9 g/L, but Mill 201 had sulfate concentrations more than twice the level found at the other mills. The chloride levels, as represented by the equivalent concentration of NaCl, ranged from less than 1 g/L to as much as 9 g/L, but no higher values were reported, since no mills were surveyed where logs are floated on seawater. In all, the compositions of minor constituents in the white liquors were also within the range generally expected in kraft pulping, with the exception of the high sulfate load encountered at Mill 201.

Polysulfides were only found in three of the white liquors analyzed for this species, and the levels detected were at the threshold of measurement for the Mead Amalgam method that was used. The highest level of excess sulfur detected was 0.24 g/L — approximately 2400 ppm.

Since make-up liquor can be considered to be a blend of raw white liquor, steaming vessel condensate, and top circulation liquor directed through the level tank, it is not surprising that the concentration of most of the inorganic species of interest was reduced in MLP liquor relative to raw white liquor. Two processes are responsible for the reduced concentrations in MLP liquors — dilution and consumption.

Raw white liquor is diluted with liquor from the level tank to form make-up liquor, and the extent of dilution can be assessed approximately by following the concentrations of a nonreactive species such as chloride. The concentration of chloride in make-up liquors is consistently 85% of the

centration in the raw white liquor. Apparently, a balance exists between the oride entering with the white liquor and leaving with the pulp/spent liquor maintain a chloride level in the make-up liquor that is approximately 85% of entering chloride concentration. The level of dilution of another relati-y inert ingredient — sulfate, Na_2SO_4 — is also approximately 85% in the liquor compared to raw white liquor. This may be considered as a dilution white liquor to form cooking liquor.

The chemical compounds which can participate in the digestion process reduced significantly below the 85% value attributed to simple dilution, parently as a result of consumption of these species in a low temperature king process. The concentration of NaOH in the make-up liquor is typically ly 65% of the concentration in the white liquor. This concentration is luced from the 85% dilution level as a result of low temperature reactions at occur in the top circulation line, the chip chute and chip chute recir-lation line, and the level tank. The temperatures in these lines are typi-lly on the order of 100°C, which is known to be high enough for cooking to cur with consumption of sodium hydroxide (6-8). Consequently, the caustic ncentration in the make-up liquor is lower than dilution alone would dictate, cause of NaOH consumption in the piping and vessels upstream of the make-up quor sampling point. This consumption reduces the NaOH concentration in MLP quor to only 65% of the white liquor value in five of six mills sampled; the maining mill retains 75% of the white liquor strength in its make-up liquor.

The sulfide consumption by low temperature cooking was expected to be ch lower than caustic consumption (6,9-10), and this was borne out in the emical analysis of MLP liquors. The concentration of Na_2S in the MLP liquors s approximately 75% of the white liquor values, which is reduced from the pure

dilution figure of 85% but does not reflect the extent of cooking consumption experienced by the caustic.

The remaining compounds analyzed in the MLP liquors did not follow any trend that could be identified. Carbonate, thiosulfate, and sulfite were found to increase or decrease in MLP liquor relative to white liquor, depending on the mill and the digester conditions. The absence of a trend may be a consequence of reactions that can produce small amounts of $CO_3^=$, $SO_3^=$, and $S_2O_3^=$ as reaction products during low temperature cooking, which will offset any changes in concentration due to mixtures of liquors. Alternatively, the precision of the chemical analysis method may not be sufficient to resolve small changes in concentration of these compounds.

The liquors extracted from the top circulation line generally resembled the make-up liquors, except for a small reduction in caustic and sulfide caused by additional low temperature cooking. In most cases, the concentration of NaOH in the top circulation liquor was 10 to 15 g/L lower than in the make-up liquor. The concentration of Na_2S was also reduced in the top circulation liquor relative to make-up liquor, but only by 2 to 4 g/L. The changes in the remaining compounds analyzed were relatively small.

Top circulation liquors were compared with impregnation zone liquors in two mills to determine the extent of cooking chemical consumption between these two zones.

In Mill 201, there was little difference in composition between liquors extracted from the top circulation line and the impregnation zone. The continuous digester at this mill was a two-vessel system and the impregnation zone

quors were extracted from the top of the impregnation vessel. This two-vessel rangement discouraged intermingling of hotter liquors from the cooking zone, id there was little difference among make-up liquor, top circulation liquor and pregnation zone liquor at this mill.

Liquors sampled from the impregnation zone of the vessel at Mill 212 owed evidence of additional consumption of caustic and, to some extent, ulfide, relative to the top circulation liquor. The NaOH concentration in the npregnation zone was consistently 10 to 15 g/L below the top circulation con- entration. The sulfide concentration was also lower in the impregnation zone, y 2 to 4 g/L. The greater extent of low temperature cooking during passage com the top separator to the impregnation zone may be attributed to higher tem- eratures caused by carryover from the adjacent high-temperature cooking zone in nis single vessel digester.

In all cases, the upper cook circulation liquors were depleted of much f the caustic entering the impregnation zone, but much of the sulfide emained. The NaOH concentration was reduced to levels ranging from 14-22 g/L y the cooking processes occurring in the impregnation zone. Only 25% of the austic entering with the make-up liquor remains in the upper cooking zone. On he other hand, 13 to 23 g/L of Na_2S remained in the upper cooking zone liquor, hich is approximately 60% of that entering with the make-up liquor. As iscussed previously, sodium hydroxide participates much more readily in low emperature cooking processes than sodium sulfide, with a greater consumption of he caustic observed as a result.

Changes in the major constituents of cooking liquors are shown chematically for the five mills in Fig. 2-6. A similar plot for the minor

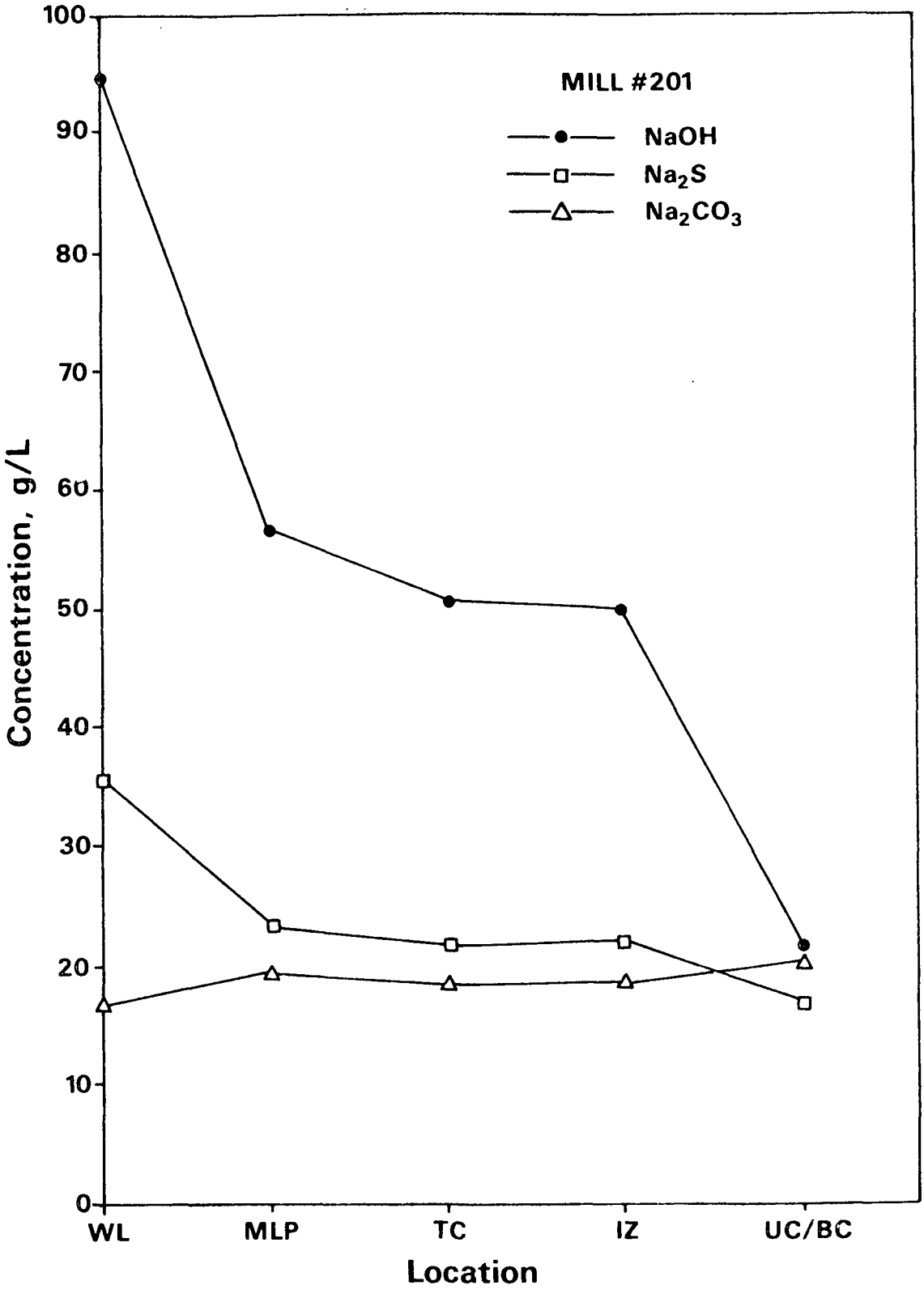

Figure 2. Schematic diagram showing variations in major constituents at Mill 201.

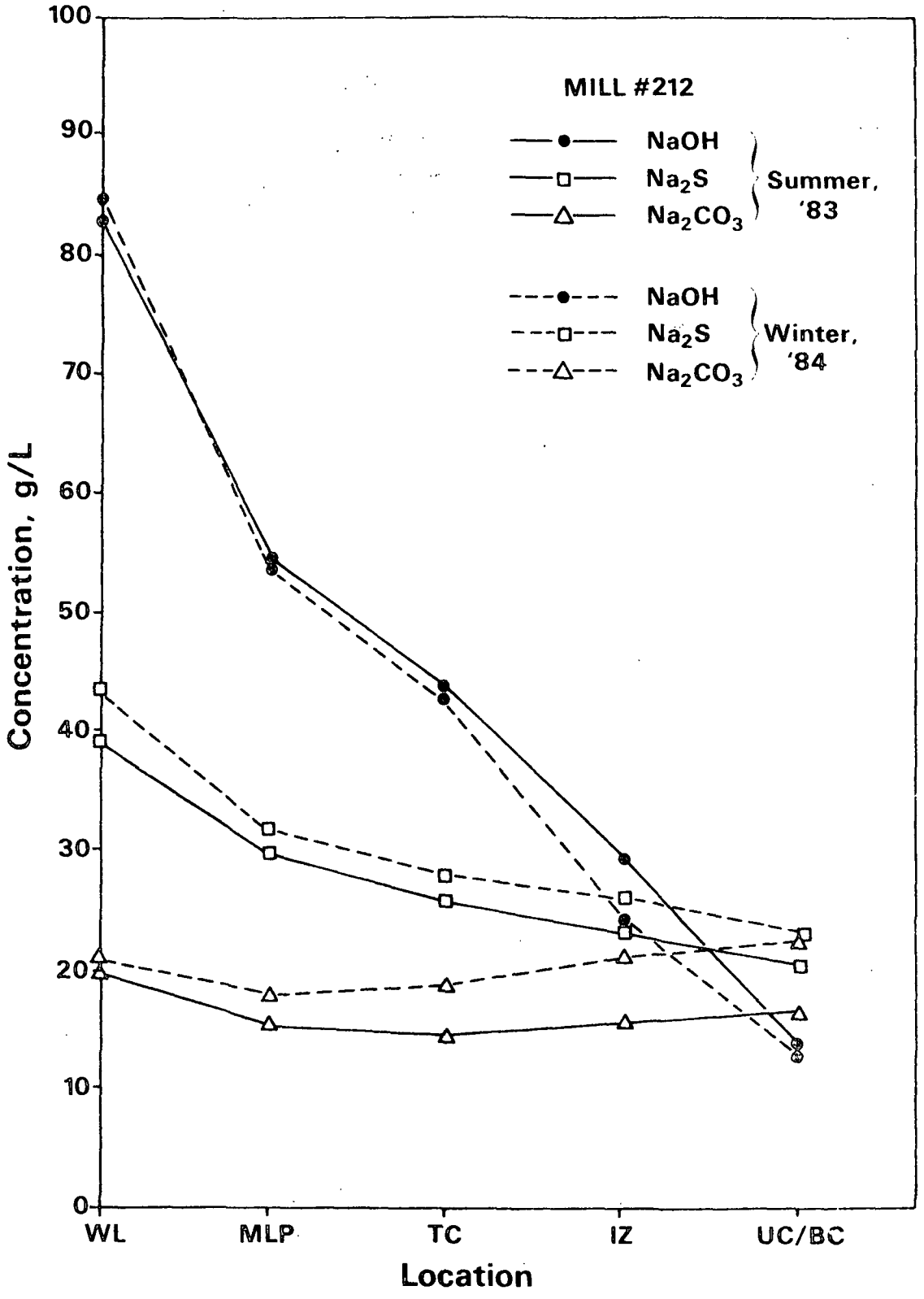

Figure 3. Schematic diagram showing variations in major constituents at Mill 212.

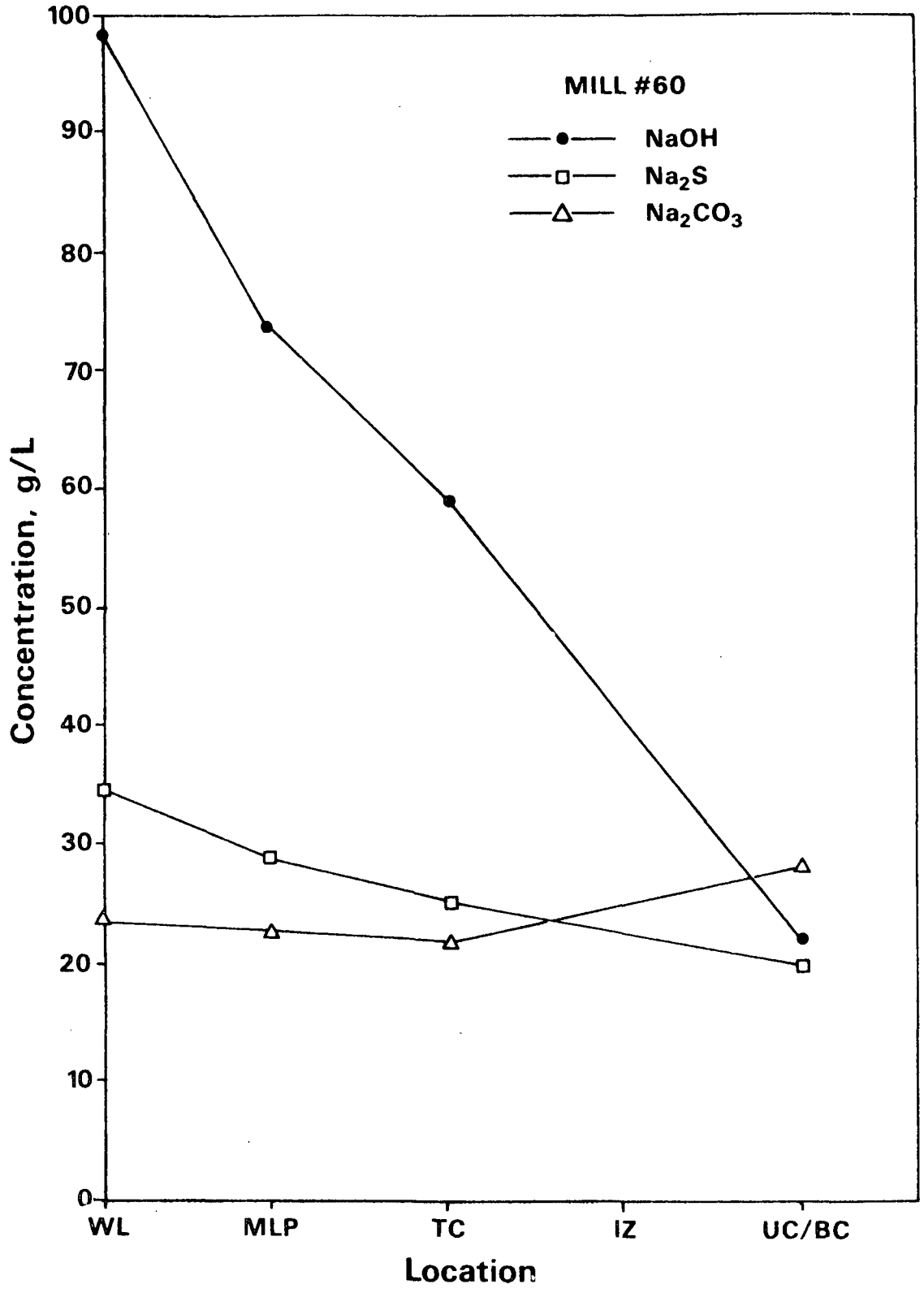

Figure 4. Schematic diagram showing variations in major constituents at Mill 60.

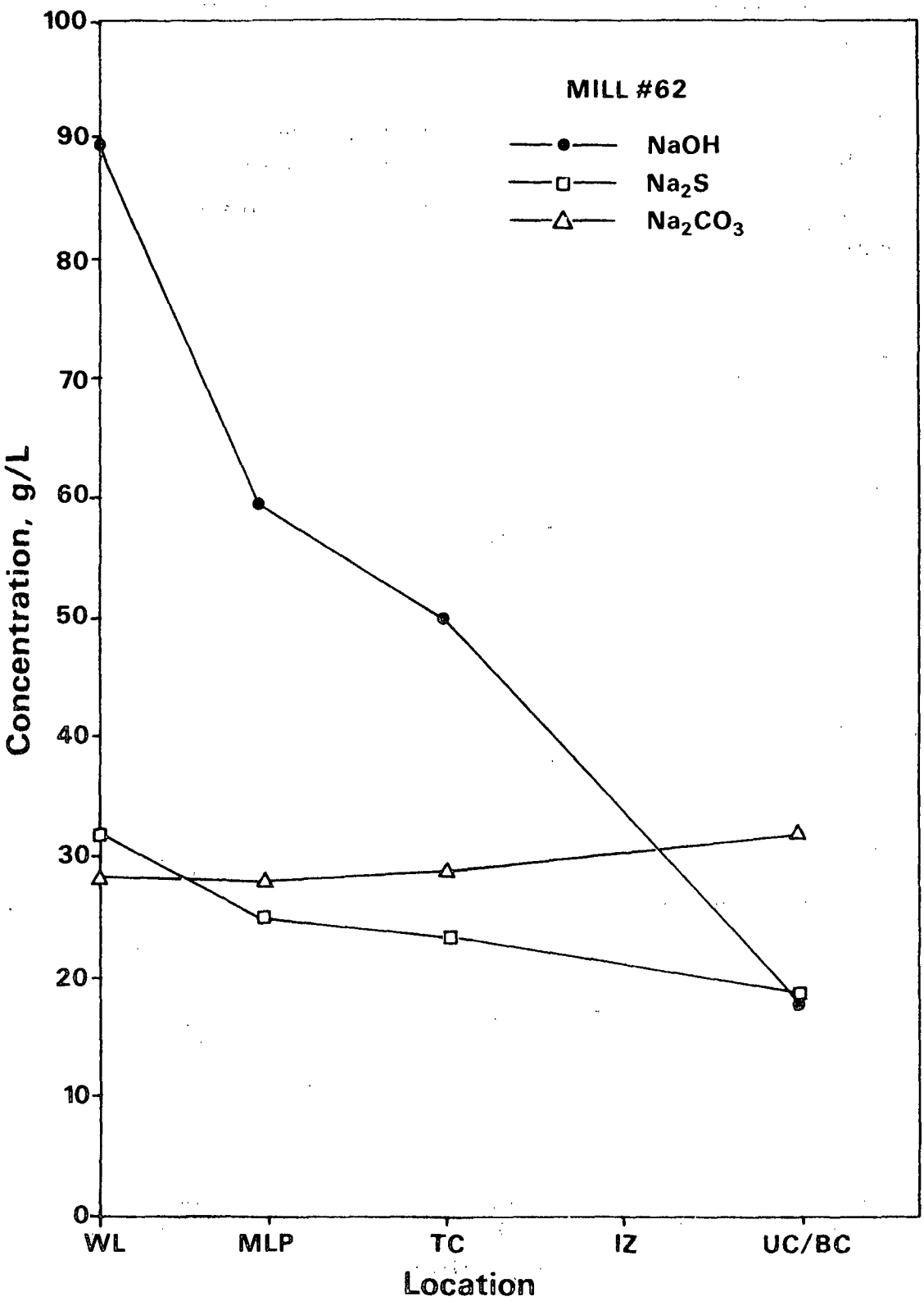

Figure 5. Schematic diagram showing variations in major constituents at Mill 62.

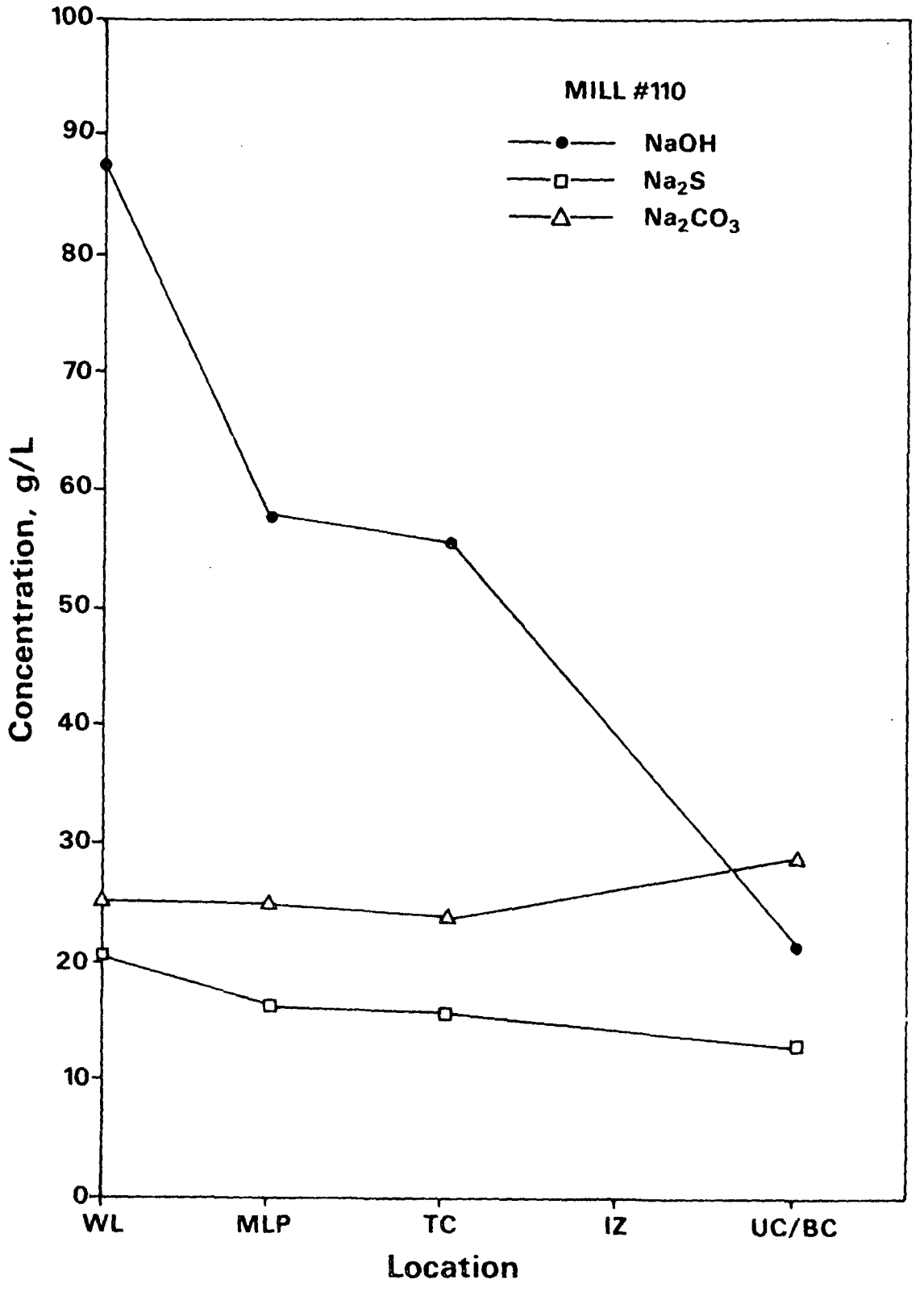

Figure 6. Schematic diagram showing variations in major constituents at Mill 110.

onstituents would show relatively little change in the concentration of these pecies, progressing from the MLP liquor to the upper cook zone liquors. Either he minor constituents do not participate in the low temperature cooking that ›ccurs in the impregnation zone, or the rate of consumption of these compounds is more or less equal to the rate of production.

Insofar as comparisons can be made, the results of the supplementary study reported here agree well with the results of the earlier survey. Table 5 compares the inorganic compositions of MLP liquors extracted at Mills 60, 62, and 110 in 1982 and 1983. There is relatively good agreement between the concentrations of major and minor constituents in liquors obtained 18 months apart.

Table 5. Comparison of liquors sampled in 1982 and 1983.

Averaged values (grams chemical/liter)

	Mill	NaOH	Na_2S	Na_2CO_3	NaCl	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4
WL (1983)	60	98.6	34.8	23.9	3.2	7.8	8.5	8.3
WL (1982)	60	102.0	35.5	30.5	2.8	7.0	3.9	23.6
MLP (1983)	60	73.4	28.8	22.3	2.8	8.1	9.4	9.8
MLP (1982)	60	75.2	27.6	25.3	2.4	7.3	3.4	17.9
WL (1983)	110	87.5	20.6	25.1	8.9	4.4	3.8	5.8
WL (1982)	110	95.4	19.4	22.6	--	--	--	--
MLP (1983)	110	58.0	16.7	25.1	7.4	4.3	3.3	5.7
MLP (1982)	110	58.3	15.1	23.2	6.5	5.5	3.1	6.4
MLP[a] (1983)	62	60.0	25.4	28.5	5.3	4.9	1.7	4.0
MLP (1982)	62	62.3	21.6	23.3	5.7	5.0	4.6	4.9

[a]Actual sampling site was the chip chute recirculation pump suction.

A comparison of the inorganic composition of liquors taken from Mill 212 in the summer and winter seasons failed to reveal differences that could be responsible for seasonal differences in cracking susceptibility. The composition of the liquors taken in May and January are summarized in Table 6. The sulfite concentration of the winter liquor is somewhat higher than the summer liquor, but this difference does not endure into the top circulation line or the digester vessel. Otherwise, the liquors taken at six-month intervals appear to be virtually identical.

Table 6. Comparison of summer and winter liquors — Mill 212.

	WL		MLP		TC		IZ		UC	
	May	Jan.	May	Jan.	May	Jan.	May	Jan.	May	Jan.
NaOH, g/L	81.1-85.1	83.8-85.6	53.7-56.1	52.9-54.9	43.2-45.1	42.5-43.9	27.2-32.7	24.7	13.1-16.2	13.2-14.1
Na_2S	36.7-41.9	42.5-45.0	28.1-31.6	31.1-33.4	24.9-27.6	27.8-29.5	22.8-24.5	26.3	19.3-21.8	22.4-23.2
Na_2CO_3	16.6-20.7	18.4-23.9	13.9-17.2	16.3-20.7	13.4-16.5	16.3-22.8	14.2-17.1	21.5	15.6-18.0	22.3-23.9
Na_2SO_3	6.0- 7.3	10.7-11.1	5.3- 8.4	5.6- 8.7	7.7- 8.7	5.1- 6.2	7.1- 9.2	7.6	4.2- 7.8	3.4- 4.9
Na_2SO_4	5.4-13.0	4.7- 6.0	5.3- 9.9	3.9- 6.4	4.8-10.6	3.9- 4.3	5.1-10.2	4.8	3.8- 8.4	3.0- 3.7
$Na_2S_2O_3$	5.0- 6.1	7.4	4.4- 5.7	6.4- 7.4	5.0- 6.1	4.9- 6.4	5.6- 8.5	7.3	4.7- 7.0	4.6- 5.3
NaCl	0.7- 0.8	0.7	0.5- 0.6	0.5- 0.7	0.4- 0.5	0.5- 1.0	0.5	0.6	0.4- 0.5	

DISCUSSION

LIQUOR VARIATIONS IN THE KAMYR PROCESS

The liquor composition at the three mills considered in both the earlier study and the current investigation were in relatively good agreement, as shown for Mills 60, 62, and 110 in Table 5. Mill 60 was experiencing a high sulfoxy compound carryover during the 1982 sampling, which was corrected by the time of the 1983 sampling event. Excluding this discrepancy, there is good agreement between the major constituent compositions for the two years, and acceptable agreement between the minor constituents for the two periods. These results indicate the constancy of pulping conditions and the continuity of analytical chemistry procedures.

With the exception of Mill 110, which has traditionally run with lower sulfidity, the five mills all used white liquor with AA in the range 95-105 g/L and sulfidity in the range 28 to 35% (based on AA). Thus, the relative uniformity of pulping conditions demonstrated in the previous study was also evident in the second phase, wherein liquors from two additional mills were sampled.

An examination of the composition of the liquors extracted from the digester process stream shows a reduction in concentrations due to both consumption of chemicals by low temperature cooking and by dilution from moisture in wood, presteaming condensate, etc. Consumption can be distinguished from dilution by considering changes in compounds that remain more or less independent of the pulping process. For example, sulfate is not considered to be a product of the low temperature pulping reaction (9), so changes in Na_2SO_4 concentration are attributed to dilution effects. Unfortunately, the resolution of sulfate analysis is not great enough to yield an unequivocal measure of dilution, since the scatter in any measurement is on the same order as the changes in composition.

However, the changes in sulfate concentration provide some measure of the overall dilution of white liquor up to the upper cooking zone region of the digester. The white liquor appears to undergo a 20% dilution by the time it reaches the upper cook zone, with most of the change occurring at the site of mixing of liquor and presteamed chips and condensate —, i.e., at the make-up liquor pump and the top recirculation line.

Hydroxide. Significant consumption of hydroxide occurs in the low temperature cooking process that occurs when chips are brought into contact with the cooking liquor, in addition to the dilution noted above. As a result of contact with wood chips, both the make-up liquors and the top recirculation liquor had lost from one-third to one-half of the NaOH present in raw white liquor. This change is much larger than the apparent dilution effect, and is attributed to the rapid low-temperature cooking reactions involving cleavage of α-aryl ether bonds in phenolic units, consumption of extractives, and dissolution of acetyl groups of hemicellulose as acetate, all of which consume hydroxide ions (7,8).

Hydroxide consumption continues at a reduced rate until the upper cook zone is reached. In some cases, this initial OH^- consumption can be quite small, as in the case of the impregnation vessel in the two-vessel system at Mill 201, where the impregnation temperatures are presumably low and cooking kinetics are slow because of the absence of heating in or adjacent to the impregnation region. On the other hand, the reduction in NaOH concentration in liquor passing from the top circulation line to the impregnation zone can be higher in single vessel systems where the impregnation region communicates with the upper cook zone heating and temperatures are higher. Under these conditions, as much as 20 g/L of NaOH can be consumed in the short time of passage from the top separator to the top of the impregnation zone.

Thus, depending on the system design and the impregnation zone temperature, the NaOH concentration in the liquor at the impregnation zone is expected to be 10 to 20 g/L below that encountered in the make-up liquor or the top recirculation liquor. This is significant because there appears to be an OH^- concentration below which caustic cracking will not occur (1).

It should be recognized, however, that the actual change in hydroxyl ion concentration may not be as large as suggested by the numbers given above because of a buffering effect of sulfide hydrolysis. As OH^- is consumed by reaction with the wood, the $S^=$ hydrolysis reaction producing hydrogen sulfide ion, HS^-, is favored via

$$S^= + H_2O \rightarrow HS^- + OH^- \quad . \qquad (1)$$

The pK value for this reaction is 10 to 13, depending on the temperature. This reaction will produce additional OH^- to replace the hydroxyl ion lost to the pulping reaction, with replacement of sulfide by hydrosulfide. This hydrolysis reaction is not apparent in the acidimetric titration for NaOH and Na_2S, since all S(II) ions titrate identically and both HS^- and $S^=$ are reported as Na_2S. Thus, depending on the consumption of hydroxyl ions, a fraction of the sulfide reported will actually be present in the liquor as HS^-, with liberation of an equivalent molar amount of OH^-.

The exact concentration of hydroxyl ions at impregnation zone temperatures is difficult to estimate from acidimetric titration results because of uncertainties in the activity coefficients for the species involved. A further complication is uncertainties regarding the equilibrium constant for reaction (1) above (11-14). Gustaffson and Tormund (15) have shown that complete hydrolysis via reaction (1) is probable at temperatures as high as 170°C in

iquors in contact with organic material. However, the molar concentration of ydroxyl ions in the impregnation zone must lie somewhere between the molar concentration of NaOH and the sum of the molar concentrations of Na_2S and NaOH.

Sulfide. The concentration of sulfur(II)* ions changes little as the low temperature cooking processes proceed in passage of chips from chip chute to upper cooking zone. As discussed above, the nature of the sulfur(II) changes from $S^=$ to HS^- as hydroxide is consumed, but the principal reactions that result in sulfur consumption do not occur until the temperature rises above 130°C and lignin reactions occur. Consequently, the concentration of sulfur(II), reported as equivalent Na_2S, is reduced only by some dilution effects and a small consumption effect, but the bulk of the sulfur(II) remains in the liquor at these temperatures. This is consistent with numerous reports of the role of sulfur in the initial stages of the kraft digestion process (6-10).

Carbonate. Changes in carbonate at various positions in the Kamyr process cycle are also negligible, once the dilution of raw white liquor has occurred. Carbonate is not a natural reaction product of the low temperature pulping processes that occur in or before the impregnation zone (16). Some losses of carbonate may occur as a result of precipitation and removal of calcium carbonate in the pulp mass, due to the retrograde solubility of this compound, but the overall level of carbonate appears to be unchanged. This also is the expected behavior for carbonate in the initial stages of the kraft digestion process (16).

Sulfite and Thiosulfate. The variation in concentrations of the minor sulfoxy compounds, Na_2SO_3 and $Na_2S_2O_3$, is slight and without an apparent trend

*Sulfur(II) ions refers to all sulfur ions in the -2 valence state in white liquor. It is the sum of HS^- and $S^=$ concentrations.

as liquors pass from raw liquor inlet to the upper cook zone. The variations that do occur are attributed to the limited resolution of the analytical technique, rather than actual changes in composition of these compounds. The concentrations of these compounds are not expected to change since they are considered to be spectator compounds, rather than participants, in the low temperature pulping processes occurring at this stage in the Kamyr process (6-10).

Negligible concentrations of polysulfide were detected in some of the raw white liquors, but in no case did the concentration of polysulfides persist into the digester liquors. The highest concentration of polysulfide was detected in raw white liquor at Mill 60, at a level of 0.2 g/L as S°. No polysulfide was detected in any make-up liquor, top circulation liquor, impregnation zone liquor or upper cook zone liquor.

The absence of polysulfide in these zones is not unexpected. Only low levels of polysulfide were detected in the first investigation of the liquor compositions in the initial study. Furthermore, the stability of polysulfide in contact with sulfite is limited by the equilibrium reactions of the type

$$Na_2S_2 + Na_2SO_3 \rightleftharpoons Na_2S + Na_2S_2O_3 \qquad (2)$$

which is heavily biased to the right (16). Polysulfides also undergo a disproportionation reaction of the type

$$S_xS^{--} + (x-1)\ OH^- + (1 - \tfrac{x}{4})\ H_2O \longrightarrow (1 + \tfrac{x}{2})\ HS^- + \tfrac{x}{4}\ S_2O_3^{--} \qquad (3)$$

according to Gustaffson and Teder (18). This reaction will cause a decomposition of polysulfide which is more extensive and proportionally more rapid when the initial concentrations of polysulfide are low and temperatures are

high. Finally, contact with organic media appears to catalyze the decomposition of polysulfide at the temperatures encountered in the top recirculation line and the impregnation zone of the digester (19).

In summary, it appears that there is a significant reduction in the hydroxide concentration as liquor passes from the raw white liquor inlet to the upper cook zone. The other compounds present in the cooking liquor are not significantly affected, once the initial dilution of white liquor by wood moisture and steaming vessel condensate is achieved.

LIQUOR SAMPLING CONSIDERATIONS

One of the principal objectives of this supplementary study was to determine whether liquors sampled from other sites in the Kamyr process stream resemble liquors found at the impregnation zone where cracking is prevalent. This is a significant issue, since there are accessible sites for liquor sampling at points in the make-up liquor line and the top recirculation line, whereas liquor sampling from the impregnation zone will generally require installation of a nozzle for sampling access.

Once the initial dilution of raw white liquor has been completed, the only compound that was found to change concentration was the hydroxide. The remaining compounds, sulfide, carbonate, sulfoxy compounds, and chloride do not vary significantly at the various sites where samples were taken — the make-up liquor pump suction, the top recirculation line, the impregnation zone (where available) and the upper cook zone, although some slight loss of sulfide was detected at the higher temperatures associated with the upper cooking region. For the reasons discussed above, the apparent decrease in the hydroxide composition may be misleading, since the hydrolysis of sulfide will act to buffer abrupt changes in hydroxyl ion concentration.

In Mill 201, where a two vessel system was in operation and temperatures in the impregnation zone were presumably lower, the differences in liquor composition at the MLP, TC, and IV sites are quite small. In this mill, liquors sampled at the top recirculation line vent adjacent to the top separator, or at the suction of the make-up liquor pump, are quite similar in inorganic compounds composition to liquors present in the impregnation zone (at the top of the impregnation vessel). A 50% reduction in NaOH level is found at the bottom of the impregnation vessel, however, indicating that significant consumption of caustic does occur in this vessel.

In Mill 212, on the other hand, there is a considerable difference in NaOH levels in the liquors taken from the MLP, the TC, and the IV locations that is evident in both winter and summer sampling events. The largest change (43 g/L NaOH to ~ 30 g/L NaOH) took place in the passage from the top circulation line to the impregnation zone. Moreover, the make-up liquor was lower in NaOH levels by approximately 10 g/L. At this mill, the caustic level indicated by the acidimetric titrations of MLP liquors is twice that of the impregnation zone. Although this change seems large, the buffering effect of hydroxyl ion generation by sulfide hydrolysis must be noted. Since this hydrolysis will produce OH^- and HS^- ions at the expense of $S^=$ ions, the impregnation zone liquor will be lower in $S^=$ and somewhat lower in OH^-, and enriched in HS^-, compared to liquors extracted from the make-up liquor suction.

As in the initial study, the organic composition of the liquors remains unknown because of limitations in analytical methods for determining organic species. However, it is known that the pulping reactions occurring at the low temperatures involved in this zone of the Kamyr system are relatively fast —— including dissolution of resins, liberation of extractives, reaction of acetyl

groups and fracture of α-aryl ether bonds (7-8). Additional pulping reactions that would liberate new organic compounds require increased temperatures and would take place later in the digestion process. On this basis, one would expect that changes in organic composition of the liquor from mill to mill would be one of degree (i.e., concentration) rather than kind.

The most conservative approach toward liquor sampling dictates actual sampling from the impregnation zone if these conditions are to be retained for analytical chemistry or for electrochemical studies. On the other hand, the general inaccessibility of these liquors presents a problem at most mills. It is reassuring to note that liquors obtained from other sites — particularly the top recirculation line vent — are generally quite similar to the impregnation zone liquors and may be used to simulate the impregnation zone liquors in spite of higher hydroxide levels. Given a choice, the top recirculation line vent is the preferred site for sampling when the impregnation zone is not equipped with a sample port. The measured differences in composition between the impregnation zone and the top recirculation line are smaller than the differences in the impregnation zone liquors at two mills, both of which have experienced severe cracking.

LIQUOR CONDITIONS IN THE IMPREGNATION ZONE

The analyses of impregnation zone liquors extracted from cracked vessels suggests that cracking can be induced in vessels exposed to liquors with nominal NaOH concentrations as low as 25 g/L. The extent of Na_2S hydrolysis at the corresponding pH and temperature is not known, but even complete hydrolysis to HS^- would only raise the OH^- concentration to the equivalent of 50-70 g/L of NaOH. If the digester cracking is caused by a caustic cracking mechanism, it

apparently proceeds at a hydroxide level that is at the lower threshold reported for caustic cracking — approximately 5% (or 50 g/L) NaOH. This near-threshold composition may account for the delays reported between digester start-up and detection of severe cracking.

The higher apparent caustic concentration in the two vessel impregnation zone may also account for the shorter incubation time between start-up and detection of severe cracking in two vessel systems. Active alkali, which is the sum of NaOH and Na_2S and may be considered to represent the potential for hydroxide formation in a liquor, is 50% higher in the liquors extracted from the two vessel impregnation zone. The cracking in this two vessel system (Mill 201) was detected earlier and found to be deeper than in the single vessel system at Mill No. 212.

The detection of low levels of active alkali in cracking digesters coincides with recent reports by Singbeil and Garner (20) who found stress corrosion cracking in liquors containing as little as 20 g/L NaOH and 20 g/L Na_2S. The corresponding active alkali level of 31 g/L Na_2O is below the lowest active alkali level (40 g/L) observed in the impregnation zone at Mill No. 212 (winter). The SSRT test used by Singbeil and Garner is a severe, accelerated test for SCC susceptibility but it shows the possibility of caustic cracking in liquors with only 30 g/L (Na_2O) of active alkali in the impregnation zone.

As indicated in the initial report, the concentration of caustic or caustic plus sulfide does not dictate the cracking behavior, since Mills 60, 62, and 110 have not experienced cracking yet the top circulation liquors have active alkali in the same range as the severely cracked vesels — 32-58 g/L Na_2O vs. 54-56 g/L Na_2O.

The conclusion regarding correlations between inorganic liquor composition and cracking susceptibility made in the initial report still appears valid. Both cracked and uncracked vessels have liquors whose inorganic compositions will support stress corrosion crack growth if the other conditions for cracking are satisfied. These remaining conditions which must also be satisfied include: a high tensile stress, a susceptible metallurgical structure, an appropriate electrochemical potential at the wetted surface, and access of liquor to the steel surface.

SEASONAL FLUCTUATIONS IN CRACKING AT MILL 212

Seasonal differences in cracking susceptibility reported at Mill 212 could not be related to the concentration of inorganic constituents in winter and summer liquors. A comparison of liquors taken at 6 months separation (Table 6) reveals little differences in the two liquors. In particular, the impregnation zone liquors taken during winter and summer seasons were quite similar in active alkali, although the winter liquor was slightly higher in Na_2S concentration and slightly lower in NaOH concentration. Differences in trace constituents also appear to be small. There appear to be no differences in inorganic composition of these liquors which would account for seasonal differences in cracking susceptibility. However, differences in organic composition of winter and summer liquors could be expected due to chip storage conditions or changes in the amount of bark pulped.

CONCLUSIONS

A supplementary program was conducted to determine liquor compositions in and adjacent to the impregnation zones of continuous digesters. The conclusions of this study are:

1. Acidimetric titrations at room temperature show that the concentration of NaOH is reduced at various sites in the following order: raw white liquor, make-up liquor, top recirculation liquor, impregnation zone liquor, and upper cook zone liquor. Other liquor constituents were approximately constant in composition in the Kamyr process, once initial dilution of raw white liquor was complete.

2. Acidimetric titrations to determine NaOH and Na_2S concentrations may be misleading because they do not consider the effects of hydrolysis of $S^{=}$ to HS^{-} as a source of hydroxyl ions during consumption of OH^{-} by low temperature pulping processes.

3. Cracking susceptibility could not be correlated to the concentration of major or minor inorganic constituents in cooking liquors. Both cracked and uncracked vessels have liquors that will support stress corrosion crack growth if tensile stress, appropriate electrochemical potential, and a susceptible microstructure are present.

4. Seasonal differences in cracking susceptibility at Mill 212 could not be related to differences in concentration of inorganic constituents of winter and summer liquors.

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